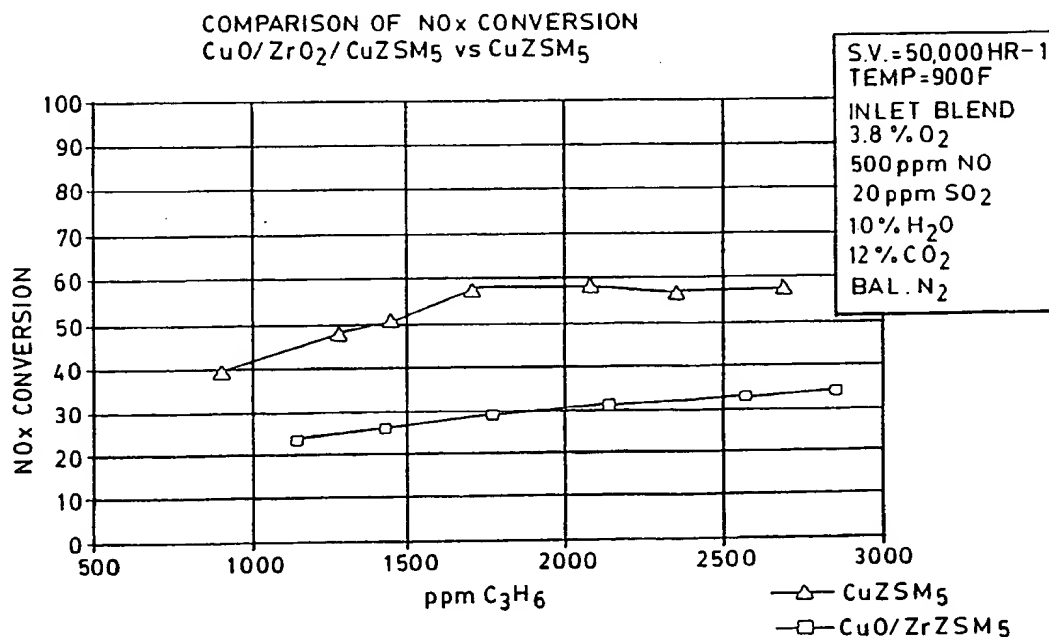




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(21) International Application Number: PCT/EP92/01882		(71) Applicant (for GB only): FORD MOTOR COMPANY LIMITED [GB/GB]; Eagle Way, Brentwood, Essex CM13 3BW (GB).	
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(30) Priority data: 753,537 3 September 1991 (03.09.91) US		(72) Inventors: MONTREUIL, Clifford ; 201 Devonshire, Dearborn, MI 48124 (US). GANDHI, Haren, Sakarlal ; 38836 Creek-Bend Drive, Farmington Hills, MI 48331 (US). CHATTHA, Mohinder, Singh ; P.O. Box 2053, Dearborn, MI 48121 (US).	
(71) Applicant (for CA only): FORD MOTOR COMPANY OF CANADA LTD. [CA/CA]; The Canadian Road, Oakville, Ontario L6J 5E4 (CA).		(74) Agent: MESSULAM, Alec, Moses; A. Messulam & Co., 24 Broadway, Leigh-on-Sea, Essex SS9 1BN (GB).	
(71) Applicant (for DE only): FORD WERKE AG [DE/DE]; Werk Köln-Niehl, Henry Ford Strasse, Postfach 60 04 02, D-5000 Köln 60 (DE).		(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE).	
(71) Applicant (for FR MC only): FORD FRANCE S.A. [FR/FR]; B.O. 307, F-92506 Rueil-Malmaison Cédex (FR).		Published With international search report.	

(54) Title: TWO-STAGE EXHAUST GAS CONVERSION CATALYST SYSTEM



(57) Abstract

This invention is directed to a two-stage catalyst system and a method of using the system for purification of exhaust gases containing nitrogen oxides, carbon monoxide and hydrocarbons. The exhaust gas may be automobile exhaust gas and invention is adapted to be useful in lean-burn situations, i.e. with oxygen rich environments. The system comprises as a first stage catalyst a combination of (i) refractory oxide impregnated with transition metal and (ii) transition metal-containing zeolite; and as a second stage catalyst an oxidative catalyst such as palladium on alumina.

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- 1 -

TWO-STAGE EXHAUST GAS CONVERSION
CATALYST SYSTEM

5 This invention is directed to a two-stage exhaust
gas conversion catalyst system comprising a first stage
reducing catalyst and a second stage oxidative catalyst.

A number of catalysts have been suggested to
convert automotive exhaust gas components like carbon
monoxide, hydrocarbons, and nitrogen oxides into other
10 gases. The nitrogen oxides present in the exhaust gas are
nitric oxide (NO) and nitrogen dioxide (NO₂), both generally
referred to by the formula NO_x. Present simultaneous
control of the three components, nitrogen oxides, carbon
monoxide and hydrocarbons, is by so-called "three-way"
15 catalysts like platinum/rhodium and palladium/rhodium.
These catalysts operate properly when the fuel mixture of a
gasoline engine is slightly "rich" and the environment is a
reducing atmosphere, i.e., in a narrow A/F ratio range
between about 14.7 and 14.4. Such three-way catalysts are
20 less than efficient in the reduction of NO_x when engines are
operated on the lean side where the A/F ratio is greater
than 14.7. It is desirable, however, to operate engines on
the lean side to realise a benefit in fuel economy,
estimated to be in the range of 5-7%.

25 U.S. patent 4,297,328 discloses a copper-containing
high-silica zeolite described as being useful as a three-way
catalyst to reduce preferentially oxides of nitrogen to N₂
on the "lean" side of the A/F mixture. High-silica zeolites
are described as those
30 preferably above 20.

Copper-containing zeolites are prone to degradation
at the high temperatures found in automobile exhaust
systems. That is, the copper tends to react with the
alumina of the zeolite and form copper aluminate which is a
35 low surface area compound with reduced catalytic activity.

The invention overcomes problems associated with
prior art catalysts and is directed to a two-stage exhaust
gas conversion catalyst system for purification of exhaust

- 2 -

gases containing nitrogen oxides, carbon monoxide and hydrocarbons. The exhaust gas may be automobile exhaust gas and the invention is adapted to be useful in lean-burn situations, i.e, with oxygen rich environments. The system
5 comprises a first stage catalyst and a second stage catalyst. The first stage catalyst is a combination of (i) refractory oxide impregnated with transition metal (ii) and transition metal-containing zeolite. The refractory oxide is selected from the group consisting essentially of
10 zirconia, silica, titania and lanthana. The second stage catalyst is an oxidizing catalyst such as a noble metal on alumina. The first stage catalyst combination may comprise an intimate mixture of refractory oxide impregnated with transition metal and transition metal-containing zeolite or
15 a layer of refractory oxide impregnated with transition metal on transition metal-containing zeolite. A preferred transition metal in the present invention is copper and the preferred refractory oxide is zirconia. Each of the catalysts may be deposited on a substrate such as a
20 honeycomb ceramic or metallic carrier or be provided in pelleted form.

The invention according to another aspect is directed to a method for the purification of exhaust gases which comprises sequentially exposing the two-stage exhaust
25 gas catalyst system disclosed above to exhaust gases of a combustion system.

The invention will now be described further, by way of example, with reference to the accompanying drawings, in
30 which :

conversions to N_2 over a wide range of hydrocarbon concentrations when using a conventional Cu-ZSM-5 monolithic
35 catalyst as compared to a $CuO/ZrO_2/Cu-ZSM-5$ monolithic catalyst according to an embodiment of the present invention.

- 3 -

Fig. 2 graphically shows a comparison of hydrocarbon conversions over a wide range of hydrocarbon concentrations when comparing the catalysts of Fig. 1.

Fig. 3 illustrates the effect of a conventional
5 oxidative catalyst placed in series (downstream) with a $\text{CuO/ZrO}_2/\text{Cu-ZSM-5}$ according to an embodiment of the present invention.

The invention is directed to a two-stage catalyst
10 system for the purification of exhaust gases containing nitrogen oxides, carbon monoxide and hydrocarbons. The first stage catalyst is placed close to the engine manifold, and converts NO_x to N_2 through a reduction reaction with hydrocarbons present in the exhaust gas stream. It also
15 converts the majority of hydrocarbons present to carbon dioxide and water and a portion of hydrogen to water. Partial conversion of carbon monoxide into carbon dioxide also occurs. The exhaust gases then pass through a second stage catalyst which further oxidizes any reducing species
20 present.

The first stage catalyst comprises a combination of two materials, refractory oxide impregnated with transition metal and transition metal-containing zeolite. This
25 combination may be in the form of an intimate mixture of the two materials or in the form of a layer of one material carrying a layer of the other, preferably a layer of refractory oxide impregnated with transition metal on top of transition metal-containing zeolite present on a substrate. Generally, the two materials of the first stage catalyst are
30 employed in a ratio between about 10% to 90% and 90% to 10% by weight. Preferably, they are employed in a weight ratio between about 40% to 60% and 60% to 40% by weight.

The refractory oxide on which the transition metal is impregnated is selected from the group consisting
35 essentially of zirconia (ZrO_2), silica (SiO_2), titania (TiO_2), and lanthana (La_2O_3), with zirconia being preferred. The refractory oxide also may comprise compatible mixtures of these oxides. The transition metal comprises, but is not

limited to, Cu, Co, Ni, Cr, Fe, Mn and compatible mixtures thereof. Transition metal is meant herein to include elemental metal as well as metal oxide. The transition metal present in the two materials of the first stage catalyst, e.g., in the refractory oxide impregnated with transition metal and the transition metal-containing zeolite may be independently selected from transition metals, i.e., one may be copper and the other be chromium. Preferably, the same transition metal or mixture of transition metals is employed in both materials. Most preferably this transition metal is copper. Optionally, but preferably, alumina is included along with the transition metal impregnated refractory oxide as a binder in amounts up to about 35% by weight based on the total weight of the alumina and the transition metal impregnated refractory oxide. According to the present invention, transition metal is not impregnated on the alumina because of its detrimental effect.

The refractory oxide impregnated with transition metal can be made by various techniques as will be apparent to one skilled in the art in view of the present disclosure. Such techniques will be discussed hereinafter with specificity to copper-containing zirconia but such techniques apply generally to other transition metal embodiments according to the present invention.

According to one method of making a copper-containing zirconia, a quantity of zirconia is soaked, repeatedly if desired, in a solution of a copper compound, subsequently dried, and then calcined at an elevated temperature between, e.g., 300-900°C, often at about 600°C. If alumina is to be incorporated as a binder, it would be mixed with the copper impregnated zirconia in a slurry prior

the transition metal-containing zeolite. The transition metal compound, in this embodiment being copper, would be one that is soluble or can be dispersed in a liquid. Particularly useful copper compounds are those which are soluble in an aqueous solution or which can be solubilized therein, e.g., with the aid of an acid or base. Exemplary

of such copper compounds are copper salts like copper nitrate and copper sulfate; organo-copper compounds like carboxylates of copper, copper acetate and copper (cupric) amines; organo-complexes of copper like diammine copper acetate; tetraamine copper sulfate, and copper acetylacetonate. Exemplary other transition metal compounds include cobaltous acetate, nickel acetate, ferric chloride, chromic nitrate and manganese acetate. Still other transition metal compounds useful in this invention to form the refractory oxide impregnated with transition metal will be apparent to those skilled in the art in view of the present disclosure.

If the calcining is carried out in air, the copper compound decomposes and forms copper oxide. If, on the other hand, the calcining is carried out in a reducing atmosphere the copper compound may be reduced to elemental copper. Preferably, the transition metal, in this embodiment being copper, is present in an amount between about 0.1 and 20% by weight in the copper-containing zirconia. When the first stage catalyst is placed in use, oxygen present in the exhaust gas will oxidize the copper to copper oxide.

In addition to the refractory oxide impregnated with transition metal, the first stage catalyst comprises a second material, transition metal-containing zeolite. The zeolite are selected from high silica zeolites having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio which exceeds about 10 and preferably about 20. Representative of such high-silica zeolites are "silicalite", ZSM-5, ZSM-8, and ZSM-11. Examples of such zeolites and methods of making are disclosed in U.S. patent 4,297,328 to Ritscher et al which is hereby expressly incorporated by reference for such teachings. It is to be understood that other zeolites having the properties described herein may be used without departing from the scope of the present invention. Silicalite is a novel crystalline silica composition having a hydrophobic/organophilic characteristic which permits its use for selectively adsorbing organic materials preferentially to

- 6 -

water. Silicalite is more completely described in U.S. patent 4,061,724 which is hereby expressly incorporated by reference for such teachings. A zeolite in the protonated (acid form) may also be used. The diameter of the zeolite particle is not limited to any particular size. Smaller particle sizes are preferred as providing more uniform coatings on the catalyst support than those of larger particle size.

The transition metal such as copper is provided into the zeolite by ion exchange. Generally a sodium zeolite is contacted by an aqueous solution of another cation, in this case an aqueous solution of a soluble copper compound such as copper acetate wherein replacement of the sodium ion by copper ion takes place. It is advantageous to provide as much transition metal ion in the zeolite as possible since the amount of transition metal present in the zeolite is directly related to the catalytic activity of the first stage catalyst. After replacing the sodium ion with metal ion, the zeolite is generally washed to remove excess surface transition metal compound. It is not necessary to do so, however.

The first stage catalyst may be made by grinding each of the copper-containing zirconia and the copper-containing zeolite to a fine powder, mixing them together, forming a slurry of them and then applying the slurry to a substrate such as metal or ceramic honeycomb. While it is preferable to make the first stage catalyst this way, according to another embodiment it may be made by layering one material onto the other. For example, a layer of the copper-containing zeolite may be applied to the substrate and then a layer of copper-containing zeolite may be applied

also be incorporated in forming the first stage catalyst, including the alumina discussed herein.

It has been found that while copper-containing zeolite displays three-way catalyst activity, the copper has a tendency with use to react detrimentally with the alumina at high temperatures. As a result of this reaction copper

- 7 -

aluminate is formed which is a low surface area compound with reduced catalytic activity. No similar detrimental reaction takes place with the refractory oxides such as zirconia employed according to the present invention. It is thus believed that by employing copper-containing zirconia in addition to copper-containing zeolite, additional copper is present in the first stage catalyst which is available to act catalytically and will not detrimentally react with the alumina. This insures that the copper remains in a form that is catalytically active.

Fig. 1 gives a comparison between the reduction of nitric oxide by a $\text{CuO/ZrO}_2/\text{Cu-ZSM-5}$ catalyst (at a 33% by weight loading) according to an embodiment of the present invention and the reduction of nitric oxide by Cu-ZSM-5 catalyst (also at a 33% by weight loading), both taken over a wide hydrocarbon concentration range. Conditions between the two runs are identical. A space velocity (S.V.) of $50,000\text{hr}^{-1}$ (space velocity being defined as the volume of gas over the volume of catalyst per time) and a temperature of 900°F are used, typical of actual internal combustion engine exhaust gas compositions. The gas composition is described in the graph. As is evident, the reduction of nitric oxide by the $\text{CuO/ZrO}_2/\text{Cu-ZSM-5}$ catalyst is more efficient than that by the Cu-ZSM-5 catalyst over the entire range of hydrocarbon concentrations examined. The $\text{CuO/ZrO}_2/\text{Cu-ZSM-5}$ catalyst reaction is on the average a factor of 2 more efficient than the comparable Cu-ZSM-5 reaction.

Fig. 2 gives a comparison between the oxidation of hydrocarbon (propylene) by a $\text{CuO/ZrO}_2/\text{Cu-ZSM-5}$ catalyst and the oxidation of hydrocarbon by a Cu-ZSM-5 catalyst under the same conditions as in Fig. 1. The oxidation of hydrocarbon by the such $\text{CuO/ZrO}_2/\text{Cu-ZSM-5}$ catalyst is more efficient than that of the Cu-ZSM-5 catalyst. The $\text{CuO/ZrO}_2/\text{Cu-ZSM-5}$ reaction is on the average a factor of $2/3$ more efficient than the comparable Cu-ZSM-5 reaction, yielding essentially quantitative conversion of hydrocarbon over the entire concentration range examined.

The second stage catalyst according to the present invention comprises a conventional oxidative catalyst such as palladium on alumina which further oxidizes any reducing species present, resulting in near quantitative conversion of hydrocarbons, carbon monoxide and hydrogen. While palladium on alumina is preferred for this second stage, it is not meant to be so limited. This second stage may comprise other oxidative catalysts like Pt/Al₂O₃, Pd/Al₂O₃, Pt/Rh/Al₂O₃, and Pd/Pt/Al₂O₃. While not as preferred as the above, the second stage catalyst may comprise zeolite in place of the alumina. The metal may be provided on the zeolite by ion-exchange and/or impregnation as will be apparent to one skilled in the art in view of the present disclosure.

15

Test Procedure

The catalysts are characterized in a quartz steady-state flow reactor. Gases are blended in a manifold by means of mass-flow controllers, routed through a by-pass line to an analytical train for analysis, and then routed over the catalyst. The post-catalyst gases are then analysed to determine the extent of reaction of the various constituents. The catalyst used is in the form of a cylindrical ceramic monolith measuring 1 inch in diameter by 1.5 inches long. Total gas flow over the catalyst is 16.09 liters/min. which gives a space velocity of 50,000 hr⁻¹. An inlet temperature of 900°F is used in all tests. The composition of the gas stream used in the following examples is that shown in Fig. 3.

(a) Copper acetate monohydrate (7.8 g) is dissolved in 150 ml of acetic acid/water mixture (50:50). Zirconia, 50 g, is placed in a beaker and is impregnated with the copper acetate solution by incipient wetness technique. It takes three impregnations to finish all the

solution. The impregnated material is dried at 120°C between impregnations and after the final impregnation. It is then calcined at 600°C for four hours.

5 (b) Cu-ZSM-5, which contains 3% by weight ion-exchanged copper, is obtained from Universal Oil Products (UOP). This material is in a powder form suitable for direct use.

10 (c) A mixture of equal weight amounts of materials (a) and (b) above is ball-milled in a sufficient amount of water to make a fine slurry. The slurry is applied to a cordierite monolith in several steps to obtain 33% loading of this mixture on the monolith as a % of the aggregate weight. The final drying is carried out at 120°C for three hours and the calcination is carried out at 600°C for four
15 hours to form the first stage catalyst.

The first stage catalyst prepared above is coupled with a 1% Pd/Al₂O₃ conventional oxidative catalyst (as the second stage catalyst) to form a two stage catalyst system according to the present invention. The system is placed
20 within a testing device with the second stage downstream of the first and tested according to the described test procedure. Fig. 3 gives a comparison of conversions of nitric oxide, hydrocarbon, carbon monoxide and hydrogen which is obtained with the two stage catalyst of the example
25 as well as that of the first stage alone. As can be seen, the use of the second stage in addition to the first stage improves the oxidation of carbon monoxide and hydrogen and also hydrocarbon but to a lesser extent for hydrocarbon.

30

Example 2

Zeolite ZSM-5 (UOP) is ion exchanged by stirring with a 0.05 M solution of copper acetate. The material is filtered, washed, and ion exchanged three times. It is then
35 dried at 120°C for 3 hours and then calcined at 600°C for three hours. The product contains 2.0 % copper by weight.

A first stage catalyst is prepared according to the procedures in Example 1(c) using the Cu/ZrO₂ product

described in Example 1(a) and the material prepared in this example instead of that of 1(b). The catalyst is provided on a cordierite monolith according to the procedure of Example 1.

5 The first stage catalyst prepared in Example 2 is coupled with the conventional oxidative catalyst used in Example 1 immediately downstream to form a two stage catalyst system according to the present invention. Similar test procedures give results comparable to those of
10 Example 1 except that NO_x conversion decreases about 10% with the decreased copper loading in the zeolite.

Example 3

15 A first stage catalyst is prepared as described in Example 1(c) from a 40:60 weight mixture of the materials described in Example 1(a) and 1(b).

 The first stage catalyst prepared in this example is provided on a cordierite monolith according to the
20 procedure of Example 1. It is coupled with a Pt/Al₂O₃ conventional oxidative catalyst immediately downstream to form a two stage catalyst system according to the present invention. Test results are comparable to those of Example 1.

25

Example 4

 A first stage catalyst is made according to the procedure of Example 1. Catalyst grade -alumina (Degussa
30 Corp.) in an amount of 25% by weight based on the total weight of alumina and copper impregnated zirconia is

composition of Example 1(c) as a binder.

 The first stage catalyst prepared in this example
35 is provided on a cordierite monolith according to the procedure of Example 1. It is coupled with the conventional oxidative catalyst used in Example 1 immediately downstream to form a two stage catalyst system according to the present

invention. The initial efficiency of catalytic activity is the same as in Example 1, but deteriorates somewhat with time.

5

Example 5

Cu-ZSM-5, described in Example 1(b), is ball milled with sufficient water to form a fine slurry and then coated on a monolith to obtain 21% weight loading. The sample is
10 subsequently coated with a Cu/ZrO₂ product (prepared as in Example 1(a)) from a water slurry thereof to impart a 11.5% coating by weight on the Cu-ZSM-5 layer. The monolith so prepared is calcined at 600°C for five hours to produce the first stage catalyst.

15

The first stage catalyst catalyst as prepared above is provided on a cordierite monolith. It is coupled with a 1% Pt/Al₂O₃ conventional oxidative catalyst to form a two stage catalyst system according to the present invention. Testing gives results comparable to those of Example 1.

20

Example 6

Fifty grams of zeolite ZSM-8 (UOP) is ion-exchanged by stirring with a 0.01 M solution of nickel acetate. The
25 material is filtered, washed and ion-exchanged three more times. It is then dried at 120°C and calcined at 600°C for three hours. The product contains 3.2% nickel by weight.

A first stage catalyst is prepared as described in Example 1(c) by employing the above material and the Cu/ZrO₂
30 product from Example 1(a) in equal amounts by weight.

The first stage catalyst catalyst prepared in this example is provided on a cordierite monolith according to the procedure of Example 1. It is coupled with a 1% Pd/Al₂O₃ conventional oxidative catalyst. Test results are
35 similar to those of Example 1 except that NO conversion is approximately 75% of that of Example 1.

- 12 -

Example 7

Zirconia is impregnated with copper as described in Example 1(a) to deposit 7.5% copper by weight. This product
5 is employed to prepare a catalyst product as described in Example 1 (c).

The first stage catalyst catalyst prepared in this example is provided on a cordierite monolith according to the procedure of Example 1. It is coupled with a 1%
10 Pt/Al₂O₃ conventional oxidative catalyst. Test results are similar to those of Example 1.

Example 8

15 Fifty grams of silica are impregnated with 8.3 g of copper acetate as described in Example 1(a). A first stage catalyst is prepared from this Cu₂SiO₂ product and Cu-ZSM-5 as described in Example 1(c).

20 It is coupled with a 1% Pd/Al₂O₃ conventional oxidative catalyst. The test procedure as described in Example 1 shows the emission reductions comparable to those of Example 1.

25 Example 9

Fifteen grams of titania and 35 grams of zirconia are mixed in a beaker and the mixture is impregnated with 8.1 grams of copper acetate as described in Example 1(a). A
30 first stage catalyst is prepared following the procedure of Example 1(b) and (c). The second stage is prepared as in

are similar to those shown in Example 1.

35 Example 10

Fifty grams of zirconia are soaked in a solution of 12 grams of lanthanum nitrate in 50 ml of water. The

- 13 -

material is dried at 125°C and then calcined at 450°C for five hours. This material is impregnated with 9.7 grams of copper acetate as described in Example 1(a). With the use of this Cu/La₂O₃/ZrO₂ material and Cu-ZSM-5, the first stage catalyst is obtained as described in Example 1. This first stage is combined with the second stage described in Example 1 and is subjected to testing. The results show that NO_x, CO and hydrocarbon conversions are comparable to those seen in Example 1.

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CLAIMS

1. A two-stage exhaust gas conversion catalyst system for purification of exhaust gases containing nitrogen
5 oxides, carbon monoxide and hydrocarbons which comprises:
a combination of (i) refractory oxide impregnated with transition metal and (ii) transition metal-containing zeolite, as a first stage catalyst, said refractory oxide is selected from the group consisting essentially of zirconia,
10 silica, titania, and lanthana; and
oxidative catalyst, as a second stage catalyst, said exhaust gas being exposed to said second stage catalyst after being exposed to said first stage catalyst.

15 2. A system according to claim 1, wherein said transition metal of said refractory oxide impregnated with transition metal and said transition metal-containing zeolite are independently selected from the group of transition metal comprising copper, cobalt, nickel,
20 chromium, iron, manganese and compatible mixtures thereof.

3. A system according to claim 1, wherein the transition metal is present in said refractory oxide impregnated with transition metal in an amount between about
25 0.1 and 20 weight percent based on the weight of said refractory oxide impregnated with transition metal.

4. A system according to claim 1, wherein said combination comprises (i) said refractory oxide impregnated
30 with transition metal and (ii) said transition metal-containing zeolite in a weight ratio between about 90% to

5. A system according to claim 1, wherein said
35 zeolite has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio greater than 10.

5. A system according to claim 1, wherein said oxidative catalyst comprises a noble metal on alumina.

7. A system according to claim 1, wherein the first stage catalyst combination comprises an intimate mixture of said refractory oxide impregnated with transition metal and said transition metal-containing zeolite.

5

8. A system according to claim 1, wherein the first stage catalyst combination comprises a layer of said refractory oxide impregnated with transition metal adhered to a layer of said transition metal-containing zeolite.

10

9. A method for the conversion of exhaust gases containing nitrogen oxides, carbon monoxide and hydrocarbons which comprises sequentially exposing said first stage catalyst and said second catalyst as claimed in any one of the preceding claims.

15

10. A two-stage exhaust gas conversion catalyst system for purification of exhaust gases containing nitrogen oxides, carbon monoxide and hydrocarbons which comprises:

20

a combination of (i) zirconia impregnated with copper and (ii) copper-containing zeolite, as a first stage catalyst, said zeolite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio greater than 10; and

25

oxidative catalyst, as a second stage catalyst, said exhaust gas being exposed to said second stage catalyst after being exposed to said first stage catalyst.

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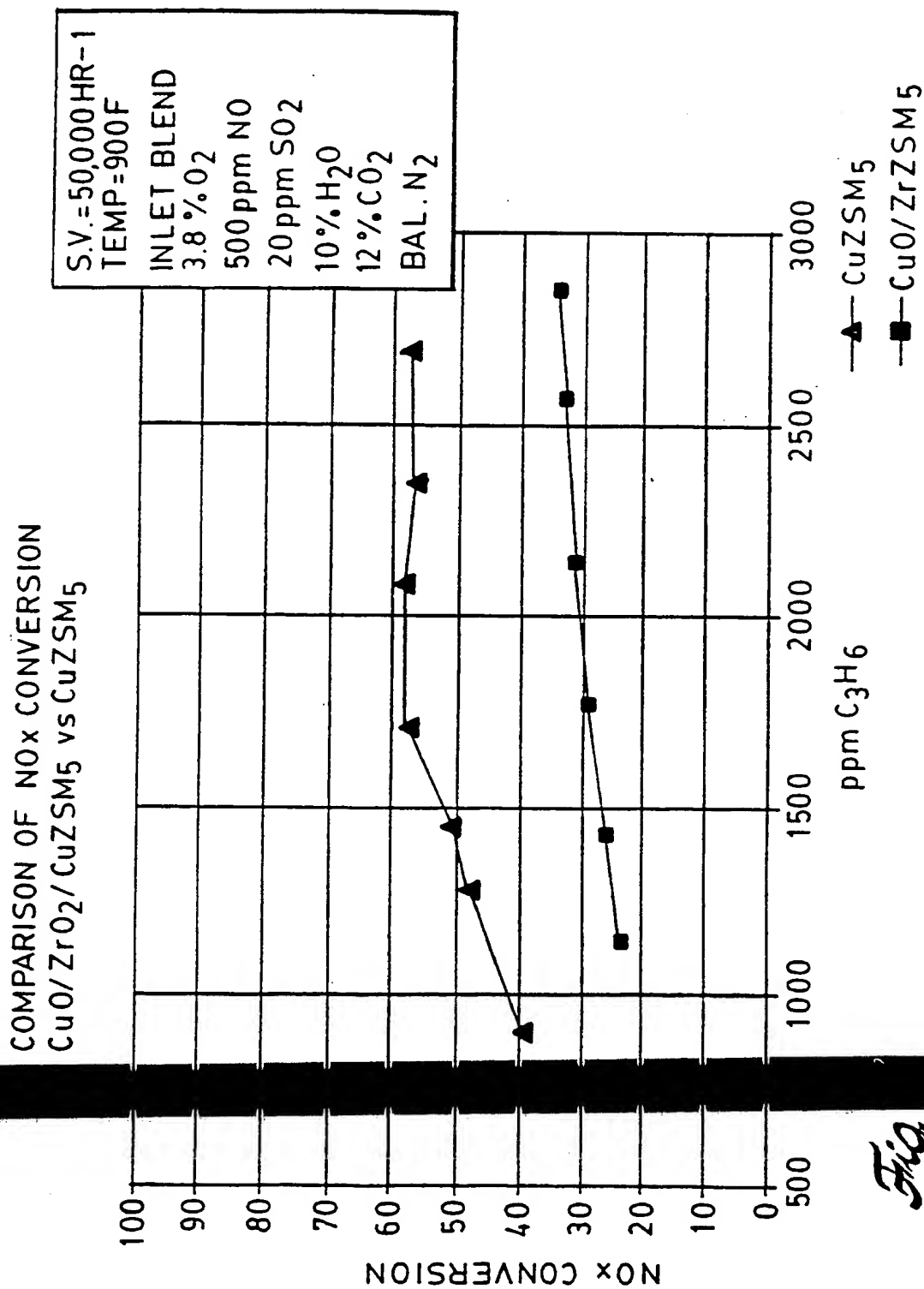


Fig.

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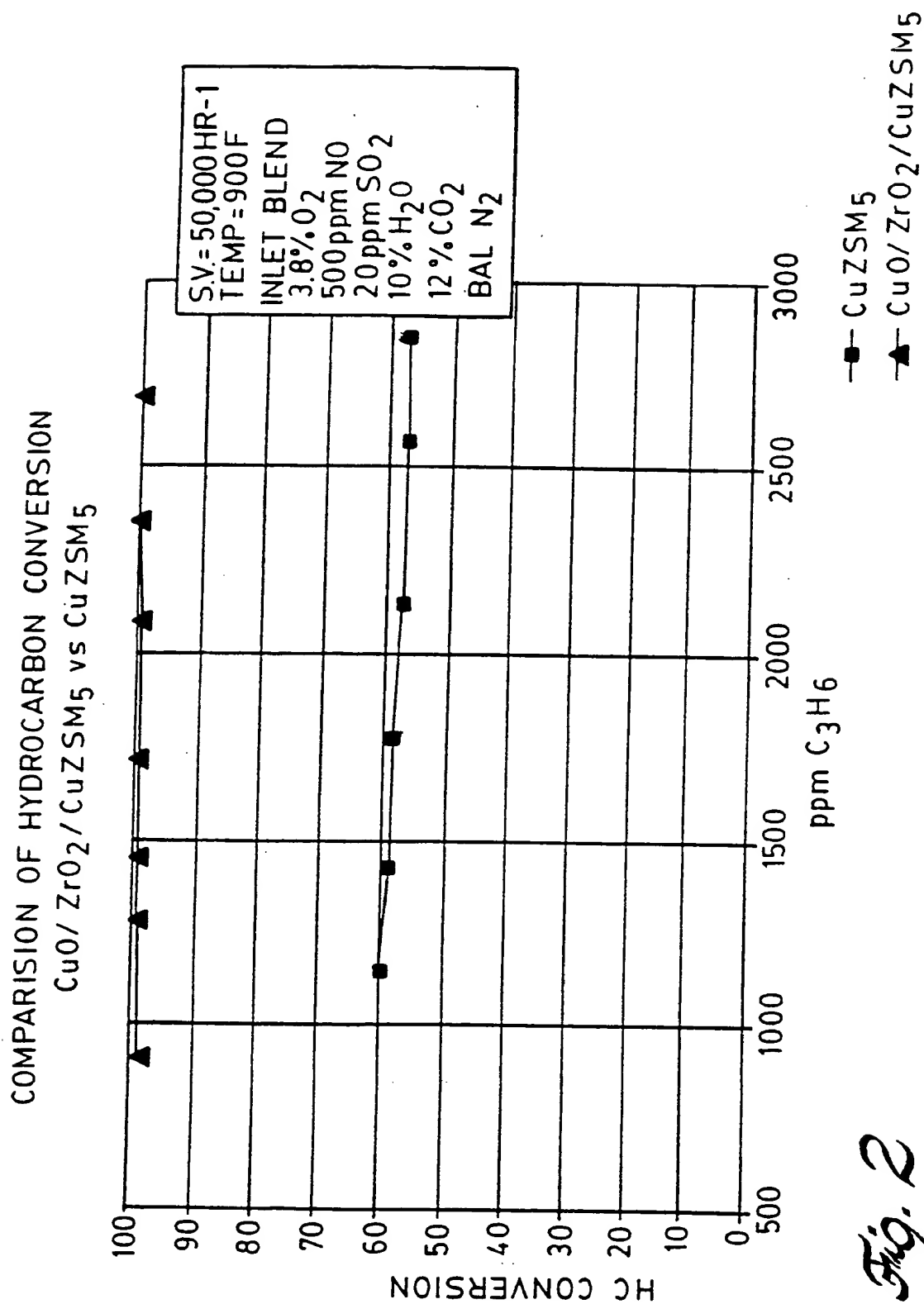


Fig. 2

3 / 3

COMPARE CONVERSIONS—CuO/ZrO₂/CuZSM₅
WITH AND WITHOUT REAR Pd COC

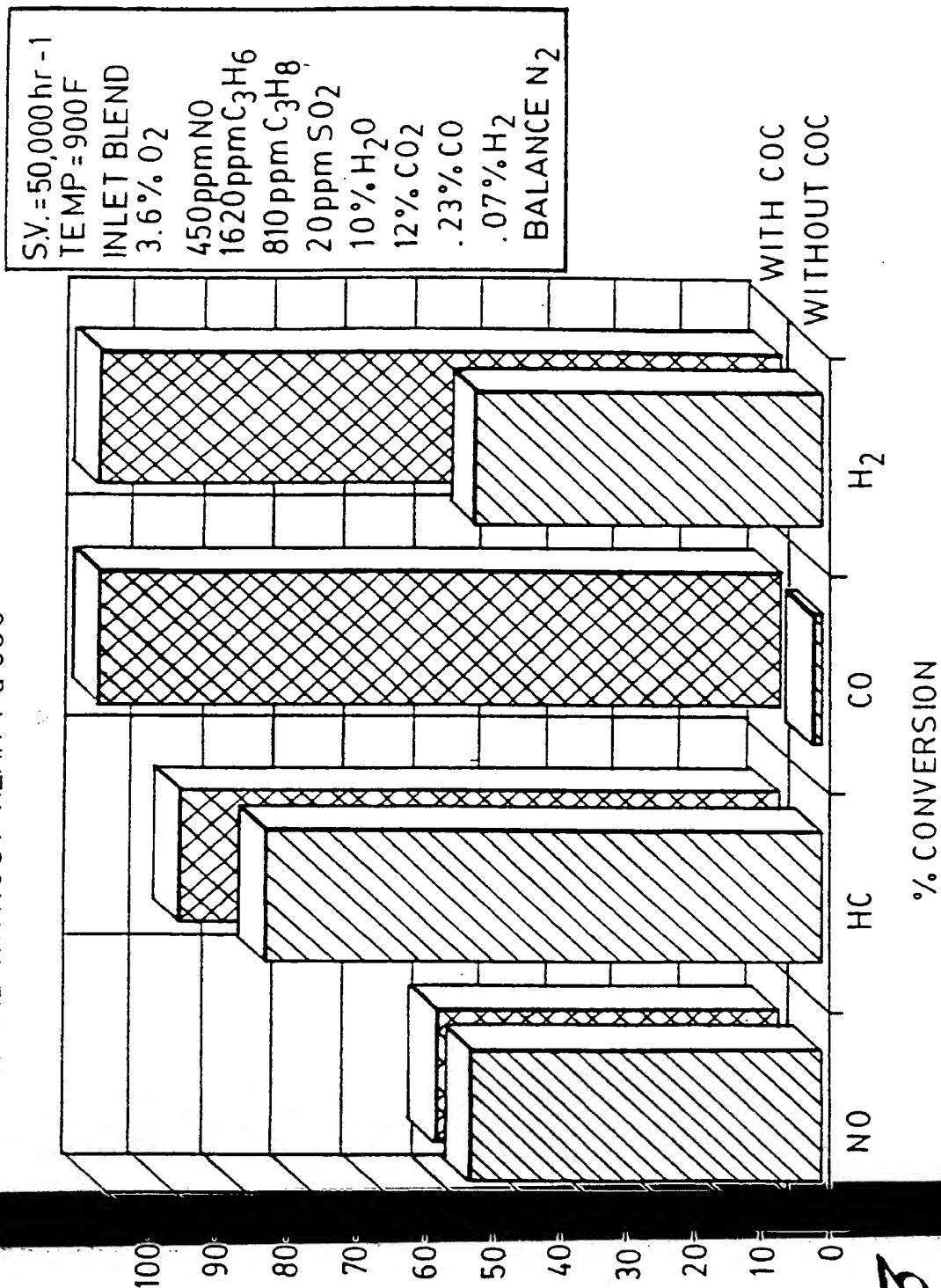


Fig 3

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 92/01882

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: B 01 D 53/36, B 01 J 29/14, 29/34														
II. FIELDS SEARCHED <div style="text-align: right; margin-right: 100px;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 30%; border: none;">Classification System</td> <td style="border: none;">Classification Symbols</td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;">IPC5</td> <td style="border: 1px solid black; padding: 5px;">B 01 D; B 01 J</td> </tr> </table> <div style="text-align: center; margin-top: 5px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched⁸</div>			Classification System	Classification Symbols	IPC5	B 01 D; B 01 J								
Classification System	Classification Symbols													
IPC5	B 01 D; B 01 J													
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category *</th> <th style="width: 70%;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 20%;">Relevant to Claim No.¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>EP, A2, 0365308 (BABCOCK-HITACHI KABUSHIKI KAISHA) 25 April 1990, see page 1, line 38 - line 45; page 2, line 4 - line 44 --</td> <td style="text-align: center; vertical-align: top;">1-10</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>US, A, 4297328 (JAMES S. RITSCHER ET AL) 27 October 1981, see the whole document --</td> <td style="text-align: center; vertical-align: top;">1-10</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>EP, A2, 0393905 (ENGELHARD CORPORATION) 24 October 1990, see the whole document -- -----</td> <td style="text-align: center; vertical-align: top;">1-10</td> </tr> </tbody> </table>			Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	EP, A2, 0365308 (BABCOCK-HITACHI KABUSHIKI KAISHA) 25 April 1990, see page 1, line 38 - line 45; page 2, line 4 - line 44 --	1-10	A	US, A, 4297328 (JAMES S. RITSCHER ET AL) 27 October 1981, see the whole document --	1-10	A	EP, A2, 0393905 (ENGELHARD CORPORATION) 24 October 1990, see the whole document -- -----	1-10
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents:¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 50%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>														
IV. CERTIFICATION <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"> Date of the Actual Completion of the International Search <div style="text-align: center;">2nd November 1992</div> </td> <td style="width: 50%; border: none;"> Date of Mailing of this International Search Report <div style="text-align: center; font-size: 1.2em;">13 NOV 1992</div> </td> </tr> <tr> <td style="width: 50%; border: none;"> International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div> </td> <td style="width: 50%; border: none;"> Signature of Authorized Officer <div style="text-align: center;">Britt-Marie Lundell</div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center;">2nd November 1992</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-size: 1.2em;">13 NOV 1992</div>	International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center;">Britt-Marie Lundell</div>								
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PCT/EP 92/01882**

SA 63549

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 30/09/92. The European Patent office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A2- 0365308	25/04/90	CA-A-	2000906	18/04/90
		JP-A-	2107315	19/04/90
		US-A-	5047378	10/09/91

US-A- 4297328	27/10/81	NONE		

EP-A2- 0393905	24/10/90	CA-A-	2012039	20/10/90
		JP-A-	2293022	04/12/90
		US-A-	5024981	18/06/91

For more details about this annex : see Official Journal of the European patent Office, No. 12/82